

ATTACHMENT OF MOLECULES WITH HIGH PERMANENT AND INDUCED
DIPOLE MOMENT TO IONS IN GASES

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ABSTRACT

The mass spectrometric study of clustered ions in function of polar gas pressure, temperature and electric field strength provides information not only on what ionic species might be present, but also on the strength of the ion-dipole interactions. Studies of the reaction $\text{H}_3\text{O}^+ \cdot (n-1)\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ in a Nier type ion source with a 100 keV proton beam are compared with earlier work on an alpha particle mass spectrometer. The residence time of the ions in the two sources are a few μsec and a few msec resp. Similarity of results shows that clustering equilibrium is established within μsec for water clusters above 0.5 torr. The presence of electric fields reduces the cluster size. 50 Volts/cm (at 1 torr) strip the clusters to H_3O^+ . Experiments on the comparative attachment of different molecules show that the stability of the attachment increases in the order H_2O , NH_3 , CH_3OH , CH_3NO_2 for first shell attachment. At larger distances from the ion (second shell) water becomes the strongest attaching. These results are explained by differences of dipole moments and polarizabilities.

INTRODUCTION

Attachment of polar molecules to ions in the gas phase occurs in a number of systems: gases under high energy irradiation, gas discharges, flames, etc. The polar molecules may be present as an accidental impurity or as a deliberate admixture. The attachment has a number of important effects such as change of mobility, change of reactivity with regard to ion-molecule reactions, change of the positive (negative) ion (electron) recombination coefficient and change in the nature of the products resulting from the positive negative ion recombination. The study of ion-polar molecule interactions in the gas phase can also provide information on ionic solvation since the formation of ion clusters constitutes the first and most important step in the solvation of an ion.

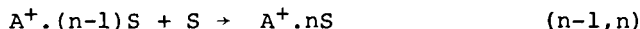
A systematic mass spectrometric study of ion-polar molecule interactions was started in this laboratory some five years ago.⁸⁻¹²

The mass spectrometric gas phase studies are based on measurement of the relative concentrations of the clustered ionic species: $A^+.nS$, $A^+.(n+1)S$, etc. The measurement of the relative concentrations is obtained by bleeding a probe of the gas into an ion mass analysis system, i.e. a vacuum chamber attached to a mass spectrometer. In the vacuum chamber the gas is pumped out while the ions are captured by electric fields, accelerated and focused and then mass analysed by some conventional means (magnetic separation quadrupole filter, etc.). After mass analysis, the ion beam intensities are detected as electrical currents.

Several types of solvation studies can be undertaken if the relative concentrations of the ionic species are known.

1. Solvation Enthalpies and Entropies of Individual Solvent Molecule Additions Steps:

Consider the ion A^+ produced in the gas phase by some form of ionizing radiation or thermal means. If the atmosphere surrounding the ion contains the vapor of a polar molecule (solvent S), a number of clustering reactions will occur.



At equilibrium the following relations will hold

$$\Delta F^\circ_{0,n} = \Delta F^\circ_{0,1} + \Delta F^\circ_{1,2} + \dots + \Delta F^\circ_{n-1,n} \quad (I)$$

$$\Delta F^\circ_{n-1,n} = -RT \ln \frac{P_{A^+.nS}}{P_{A^+} \cdot (n-1)S \cdot P_S} = -RT \ln K_{n-1,n} \quad (II)$$

where P_x is the partial pressure of X .

Thus knowledge of the equilibrium concentrations of the clustered species $A^+.nS$ obtained from experiments at different pressures of S will allow the determination of $K_{n-1,n}$ and $\Delta F^\circ_{n-1,n}$. Such measurements done at different temperatures will lead to the evaluation of $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$. The availability of such detailed information will, for instance, reveal the shell structure since a discontinuous change of the $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ values will occur whenever a shell is completed. Finally, the total heat of solvation of the ion can also be obtained from the expression III, with equations of the same form holding for the

$$\Delta H_{\text{solv}} = \sum_{n=0}^{\infty} [\Delta H_{n-1,n} - \Delta H_{\text{evap}}(S)] \quad (III)$$

free energy and entropy change of solvation.

It is evident from equation II that only the relative concentrations of the ionic species are required. Thus $\Delta F^\circ_{n-1,n}$ and K_p can be obtained from equation II by assuming that the mass spectrometrically measured ion intensities are proportional to the equilibrium partial pressures of the ions in the ion source. The solvation of NH_4^+ by NH_3 ⁹ and H_3O^+ by H_2O ¹² represent examples of studies of this type.

2. Comparative Solvation of Two Different Ions by the Same Solvent:

There are three variants of this type of study.

(a) Comparative solvation of ions A^+ , C^+ by solvent S.

The two ions are produced in the same system which also contains vapor of the solvent S. In general, depending on the effective radius and structure of the ion, the relative concentration of clusters $\text{A}^+.\text{nS}$ will be different from that of $\text{C}^+.\text{mS}$. Thus, for example, in the average n may be larger by 1 or 2 units than m. This will reveal a stronger interaction of A^+ with S. Comparison of n and m can be done at different temperatures and pressures (of S) so as to compare the interactions in the inner shell or in the outer shells. An example of this type of study is the system H_3O^+ , NH_4^+ and Na^+ in H_2O vapor which is described in a forthcoming publication.¹³

(b) Comparative solvation of ions A^+ and B^- by solvent S.

An example of this type of study would be the system K^+ and Cl^- with H_2O . Since the orientation of the water dipoles is reversed in the solvation of positive and negative ions, such a comparative study is of great interest, particularly for isoelectronic pairs as the one quoted above. We have not yet done studies on such isoelectronic pairs. However, such studies are perfectly possible. The pair K^+ and Cl^- could be produced in water vapor. By reversing the mass spectrometer controls, measurements on the positive and negative ions in the system could be done within minutes of each other.

(c) Comparative solvation of two negative ions by S.

An example of this type of study for the ions Cl^- , BCl^- , and B_2Cl^- by H_2O is given in a forthcoming publication.¹³

3. Competitive Solvation of Ion A^+ (or B^-) by Solvent Molecules of

Solvents S_1 and S_2 : A comparison of the solvating power of two different solvents can be obtained by measuring the composition of ion clusters when two different solvents are present at known partial pressures. An example of this type of study is the competitive solvation of NH_4^+ by H_2O and NH_3 which has been reported on elsewhere.⁸ Some more recent studies will be described in the present paper. These concern the competitive solvation of the proton by water and methanol. The water-methanol system is of interest since the dipole moment of water is slightly higher than that of methanol while the polarizability of methanol is considerably larger than that of water. Thus it might be expected that at close range to the central ion methanol might be preferentially solvating.

EXPERIMENTAL

The mass spectrometric study of ion solvent molecule interactions requires mass spectrometric apparatus which can sample ions originating in ion sources at relatively high pressures. Three somewhat different arrangements are presently in use in this laboratory.

1. Alpha particle mass spectrometer¹¹

A recent version of this apparatus has been described elsewhere¹³ in detail. The gas, supplied from a conventional gas handling system, is irradiated in the ionization chamber. The radiation is supplied from an enclosed 200 mc polonium alpha source. The irradiated gas bleeds through a leak into the evacuated electrode chamber. There the ions carried by the gas are captured by the electric fields while the gas is pumped away. The ions are focused, accelerated and then subjected to mass analysis and electron multiplier detection in a 90° sector field analyzer tube.

2. Electron beam mass spectrometer⁶

In a more recent apparatus an electron beam is used as ionizing medium. The ion source is identical to that used with the alpha source with the exception that the former alpha source port contains only one very thin nickel foil (10^{-5} inches) window through which the electrons enter the source. The electrons are created by an ordinary electron gun housed in a sidearm of the vacuum chamber opposite the nickel window. The electron filament is kept at some -25000 volts while the ion source is near ground potential. Absence of radioactive contamination, high intensity (~ 10 microamps) and possibilities for pulsing (for determination of ionic lifetimes) are some of the advantages of the electron beam source. A disadvantage is the much greater scattering of electrons at high ion source pressures which makes beam collimation a problem. A quadrupole mass analyzer is used with this instrument.

3. Proton beam mass spectrometer⁵

A 100 kev proton beam obtained from a Walton-Cockroft accelerator is used as ionizing medium. The ion source is not like the previous ones but of the conventional design, i.e. a rectangular box with repeller and narrowed-down ion exit slit. The proton beam enters and exits the ion source through very thin nickel foil windows (10^{-5} inches). The ion optics are of the conventional Nier type and magnetic analysis is used. A proton beam (preferably of even higher energy than used by us since at energies below 100 kev charge exchange converts appreciable fractions of the proton beam into an H atom beam) seems to be the most convenient ionizing medium for high ion source pressures since it provides high intensity, possibility for pulsing, and little scattering at high pressure. The proton beam can also be deflected electrostatically before entering the ion source. This permits variation of the proton beam - exit slit distance in the ion source. The cost of Walton-Cockroft accelerators is relatively low.

A high pressure mass spectrometer using Mev protons from a Van de Graaff accelerator has been described by Wexler.¹⁵

RESULTS AND DISCUSSION

1. Competitive solvation of CH_3OH_2^+ by water and methanol

A study of the ions in methanol vapor in the pressure range 1-10 torr showed that most of the ions belonged to the series $\text{CH}_3\text{OH}_2^+ \cdot n\text{CH}_3\text{OH}$. This suggested the possibility of observing the competitive solvation of CH_3OH_2^+ by water and methanol molecules. Figure 2 shows the relative intensities of the mixed clusters obtained when irradiating mixtures of 5% methanol: 95% water and 20% methanol: 80% water, both at 5 torr total pressure and 50°C ion source temperature. In the mixed methanol-water clusters the question of the structural assignment arises. Thus the ion of mass 119 could be assigned as $\text{H}^+ \cdot 2\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ or $\text{CH}_3\text{OH}_2^+ \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ or $\text{H}_3\text{O}^+ \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$. We have selected the notation $\text{CH}_3\text{OH}_2^+ \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$ (or $\text{CH}_3\text{OH}_2^+ \cdot m\text{M} \cdot w\text{W}$, for the general cluster where M and W stand for CH_3OH and H_2O and m and w for the number of methanol and water molecules). The proton was assigned to the methanol oxygen ion since the proton affinity of methanol is some 10-20 kcal/mole¹³ higher than that of water. This assignment is also consistent with the observation that even in mixtures where water predominates, i.e. 5% methanol, the pure hydrate $\text{H}_3\text{O}^+ \cdot w\text{W}$ was not observed, while the pure methanol cluster $\text{CH}_3\text{OH}_2^+ \cdot m\text{M}$ was observed.

The clusters obtained with 5% methanol (Figure 1) contain, on the average, considerably more methanol than water even though the partial pressure ratio of water to methanol is 19:1. Thus methanol is the stronger solvent in the observed clusters, i.e. clusters containing up to six solvent molecules. We shall be able to understand the meaning of this result better after a more detailed treatment of the data. It can be shown that the distribution of water and methanol in the observed clusters follows quite closely a probability distribution. Calling the probabilities for inclusion of water and methanol ω and μ , for a cluster with a total of ℓ solvent molecules the probability distribution will be given by the binomial expansion of the term $(\omega + \mu)^\ell$. For example if a probability distribution is followed, the cluster containing three solvating molecules $\text{CH}_3\text{OH}_2^+ \cdot m\text{M} \cdot w\text{W}$, where $\ell = m + w = 3$, should show the following relative intensities: $\text{CH}_3\text{OH}_2^+ \cdot 3\text{W} : \text{CH}_3\text{OH}_2^+ \cdot 2\text{WM} : \text{CH}_3\text{OH}_2^+ \cdot \text{W}2\text{M} : \text{CH}_3\text{OH}_2^+ \cdot 3\text{M} = \omega^3 : 3\omega^2\mu : 3\omega\mu^2 : \mu^3$. We have obtained values for ω and μ by fitting binomial expansions to the experimentally observed distribution. The calculated intensities shown in Figure 2 demonstrate that a relatively good fit of the experimental data can be obtained. In order to express the preference for inclusion of methanol and water per unit methanol and water pressure we define $\gamma = (\mu/P_M)/(\omega/P_W)$ as the factor for preferential take up of methanol, P_M and P_W being the partial pressures of methanol and water present in the ion source. The γ 's calculated in this manner are given in Figure 1. The results at 5 and 20% methanol show that the γ 's for a cluster of a fixed size (i.e. $\ell = \text{const}$) are approximately independent of the methanol-water pressure ratio. This independence was confirmed in a number of other runs with 2, 4, 5, 8, 20, 50% methanol at 2 and 5 torr total pressure. The γ 's are found to decrease as ℓ increases. Thus methanol is taken up preferentially by a factor of 55, 21 and 8 for clusters containing 3, 4 and 5 solvent molecules. Figure 2 shows a log γ plot versus the number of solvating molecules. The plot is almost linear and allows an extrapolation to log $\gamma = 0$ or $\gamma = 1$. This occurs when the cluster contains seven solvating molecules. For $\ell > 7$, γ becomes less than unity, i.e. water begins to take precedence. Figure 2 also shows results obtained with the proton beam mass spectrometer. The total pressure in these runs was much lower (0.6 torr) and the reaction time much shorter (a few microseconds versus a few milliseconds in the alpha particle ion source).

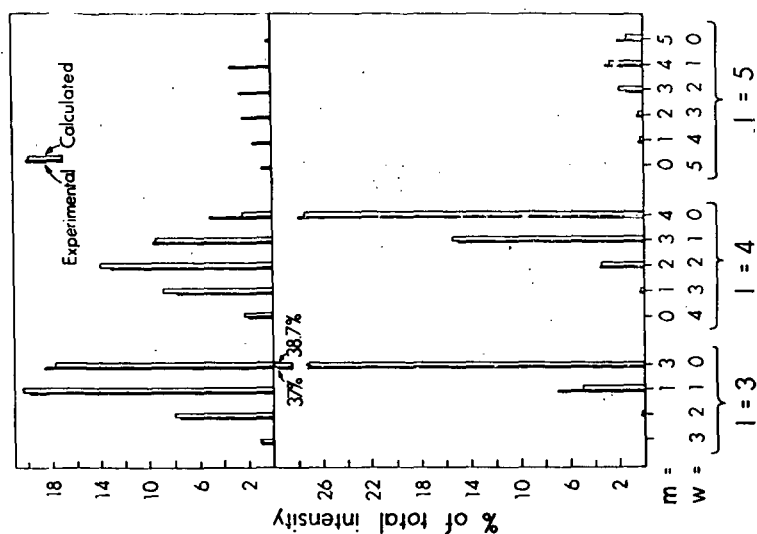


Figure 1 Mixed water and methanol content in $\text{CH}_3\text{OH}_2^+ \cdot m\text{CH}_3\text{OH} \cdot w\text{H}_2\text{O}$ clusters. Ion source temperature 50°C .

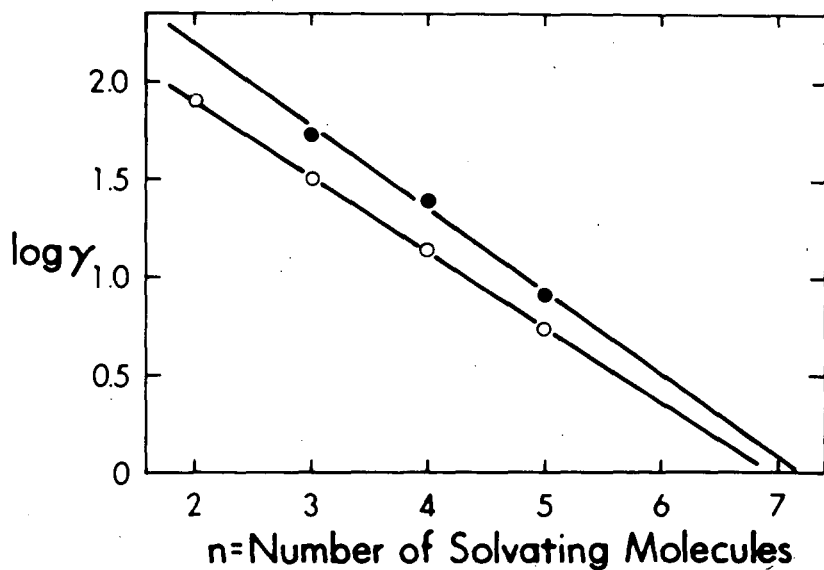


Figure 2 Plot of $\log \gamma$ versus number of solvating molecules.

γ is factor for preferential take up of methanol over water into ion $\text{CH}_3\text{OH}_2^+ \cdot m\text{CH}_3\text{OH} \cdot w\text{H}_2\text{O}$, where $m + w = n$.

One might suspect that under these conditions clustering equilibrium might not be achieved. However the results are, on the whole, quite similar to those obtained with the alpha ion source. This might be taken to mean that clustering equilibrium establishes very rapidly and that the proton beam results approach equilibrium.

In the interpretation of the present results considerable help can be obtained from the "electrostatic theory" for metal-ion coordination complexes.² It is recalled that this theory, using simple electrostatic concepts, allows the calculation of the binding energies of metal complexes in the gas phase and that the results of such calculations have been in many cases very successful. In general, the potential energy of a complex ion is built up of four terms. These are due to the attraction between the ion and the permanent and induced dipole of the ligands, the mutual repulsion of the dipoles, the energy required to form the induced dipoles and the van der Waals repulsions between the ligands and the central ion. Comparing the potential energies of an ion having water or methanol molecules as ligands, it is found that the first term is the decisive one. The first term contains the sum of the permanent dipole and the polarizability. The dipole moments of water and methanol are 1.85 and 1.69 D while the polarizabilities are 1.48 and 3.23 Å.³ The potential energy of an ion dipole interaction varies inversely with the square of the distance while the polarizability interaction depends on the fourth power. It follows that the methanol molecules with their slightly lower dipole but considerably higher polarizability will be more strongly solvating than water at close range to the ion. The experimentally observed preference for methanol is thus to be understood as resulting from the higher methanol polarizability.

It can be shown that the possibility of fitting the observed clusters with a given ℓ by a probability distribution suggests that for $\ell < 6$ all solvent molecules belong to an inner solvation shell. Suppose that for $\ell = 5$ some of the molecules went into an inner shell (fully occupied) and the rest into an outer shell. The preference for methanol over water in the inner shell will be very different from that in the outer shell. It might even be expected that water will be preferentially taken up in the outer shell. It follows that the water-methanol distribution in a cluster containing inner and outer shell molecules could not be fitted by a single probability distribution of the type $(\omega + \mu)^{\ell}$ but that the inner and outer shell would have to be fitted separately. Such a case is in fact observed in the competitive solvation of NH_4^+ by H_2O and NH_3 which was studied earlier.¹² Since the water-methanol clusters of $\ell = 3, 4, 5$ can each be fitted with a probability distribution we can conclude that these clusters do not contain molecules which occupy a distinct outer shell, i.e. that the inner shell contains at least five solvent molecules.

The ability to fit a cluster of constant ℓ with a probability distribution is, to a certain extent, surprising even if all molecules belong to the same solvation shell. A probability distribution means, for example, that in the five cluster the preference for methanol over water is the same whether all the remaining four ligands are water or methanol or a mixture of them. Obviously this can not be strictly true. The meaning of the experimental result must be that the nature of the other occupants is, in the first approximation, not important.

While γ remains approximately constant for a cluster distribution with $\ell = \text{const}$, it was observed that $\gamma_{\ell} = \text{const}$ decreases from $\ell = 3$ to $\ell = 5$. This can be understood if one assumes that whenever ℓ is increased by one unit the effective radius of the (inner) shell increases. This causes the polarizability to become less important and leads to a decrease of the preference for methanol. An increase of the effective

radius might be expected because of the mutual repulsion due to dipole and van der Waals' forces between the ligands.

Experiments on the competitive solvation of CH_3NO_2 and H_2O have also been made but this work is not yet completed. The available results show that CH_3NO_2 is taken up preferentially at close range of the central ion (NH_4^+ and H_3O^+ gave similar results). Thus at room temperature the preference factor is ~ 200 for three ligands, 60 for four ligands, 40 for five, etc. The results also seemed to show that nitromethane is always taken up preferentially in an incomplete shell (inner or outer) but that it is ultimately expelled from inner shells.

2. Effect of electric fields on cluster size

One may expect that the presence of electric fields will lead to a decrease of the average cluster size. This effect is illustrated in Figure 3. The data were obtained with the proton beam mass spectrometer which has a Nier type ion source, i.e. ion exit slit and repeller. The distance from proton beam to ion exit slit was 2.04 cm. E_r is the repeller field strength. In preliminary experiments at very low repeller fields it could be shown that at H_2O pressures higher than about 0.3 torr the cluster composition obtained with the proton mass spectrometer was very similar to that obtained with the alpha particle instrument. Since the estimated ion residence times are ~ 10 micron for the proton mass spectrometer and ~ 1 millisecon for the alpha instrument these results were taken to mean that in both instruments clustering equilibrium or near equilibrium is achieved. Figure 3 shows that increase of the electric field decreases the cluster size. This is a gradual process as shown by the succession of maxima. The maximum composition shifting successively from four water to zero water content of the H_3O^+ ion. Possibly plots of the type given in Figure 3 could be used for determination of the enthalpy of attachment, i.e. $\Delta H_{n-1,n}$.

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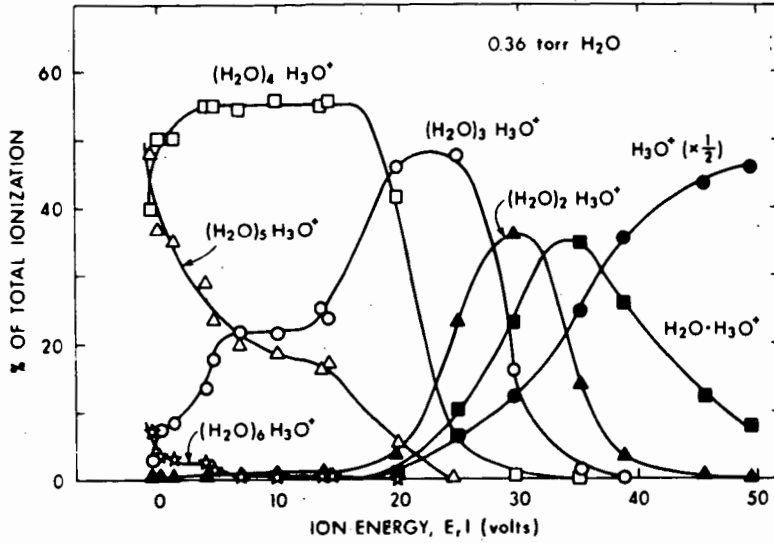


Figure 3 Effect of electric field on cluster composition. E_{rl} equals voltage between repeller and ion source exit slit. Temperature of ion source 30°C. Water pressure 0.36 torr. Experiments taken with 100 kev proton beam mass spectrometer.